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(54) METHOD FOR PREPARING SUSPENSION OF SUPERFINE METALLIC
COBALT POWDER

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PATENT SPECIFICATION

1. Title of the Invention: Method for Preparing Suspension of Superfine Metallic
Cobalt Powder

2. Claims:

(1) A method for preparing suspension of a superfine metallic cobalt powder by subjecting a cobalt carbonyl compound to thermal decomposition in an organic solvent, said method being characterized by using a reactor made from an inert material.

(2) The method of Claim 1, wherein said inert material is selected from the group consisting of one or more of the following compounds: tetrafluoroethylene resin, trifluoroethylene chloride, a copolymer of tetrafluoroethylene and perfluoroalkylvinylether, a copolymer of tetrafluoroethylene and hexafluoropropylene, a copolymer of tetrafluoroethylene and ethylene, a copolymer of trifluoroethylene chloride and ethylene, aluminum, stainless steel, and copper.

(3) The method of Claim 1, wherein an average grain diameter of the superfine cobalt in said superfine metallic cobalt powder suspension is within the range of 100 to 5000Å.

(4) The method of Claim 1, wherein said organic solvent is selected from the group consisting of one or more of the following: lower alkoxybenzene, substituted or unsubstituted lower aliphatic or aromatic primary alcohol, lower aliphatic or aromatic ether, lower aliphatic or aromatic ketone, acetate, glycerol ester, or ketone-substituents of the above compounds.

3. Detailed Description of the Invention

(a) Field of the Invention

The present invention relates to a method for preparing a suspension of a superfine metallic cobalt powder by subjecting a cobalt carbonyl compound to thermal decomposition in an organic solvent, the method being characterized by using a reactor made from a neutral material.

More specifically, the invention relates to a method for preparing a suspension of a

superfine metallic cobalt powder of high purity which does not form mirror-like deposits of metallic cobalt [on the inner walls of the reactor] and is free of any adsorbed layers of organic polymer compounds and cobalt oxide layers on the surfaces of superfine particles of the metallic cobalt.

A superfine metallic cobalt powder is a valuable material that finds application in various fields such as superconductive materials, magnetic wave absorbers, photosensitive materials, semiconductors, materials for powder metallurgy, catalysts, etc.

(b) Description of the Prior Art

A method for preparing a suspension of a superfine metallic cobalt powder by subjecting a cobalt carbonyl compound to thermal decomposition in an organic solvent is known and described, e.g., in Japanese Patent Publication (Kokoku) S40-3415.

(c) Problems to be Solved by the Present Invention

According to Kokoku S40-3415, the method of preparation of a superfine metallic cobalt powder suspension involves addition of an organic polymer compound with a molecular weight exceeding 4000. This results in increase of viscosity of the obtained suspension and creates problems associated with removal of the organic polymer compound that is absorbed by the superfine metallic cobalt particles. Furthermore, the superfine cobalt powder produced by the above method could not be utilized in applications where presence of an organic polymer compound is undesirable.

On the other hand, as the authors are aware of, preparation of the fine powder cobalt suspension without addition of an organic polymer compound is associated with formation of a mirror-like deposit of metallic cobalt on the materials of stirrer, reactors, and the like. This phenomenon is especially noticeable in the case of glass, and even though the above method allows obtaining of a superfine metallic cobalt powder suspension, the cobalt precipitated in a mirror-like deposit is peeled off from the surface, mixed with the superfine metallic cobalt powder, and thus deteriorates purity of the obtained suspension.

(d) Means for the Solution of the Problem

As a result of study aimed at the solution of the problems inherent in the prior-art method with thermal decomposition of a cobalt carbonyl in an organic solvent, the authors have found that a cobalt powder of high purity, which does not contain mirror-like deposits of metallic cobalt and is free of any adsorbed layers of organic polymer compounds and cobalt oxide layers on the surfaces of superfine particles of the metallic cobalt, can be obtained if working surfaces of stirrers, reactor, and other units of the equipment are made from an inert material which is free of polar groups.

Cobalt carbonyl compounds suitable for the purposes of the present invention may comprise hydridotetracarbonyl cobalt $\text{HCo}(\text{CO})_4$, octacarbonyl dicobalt $\text{Co}_2(\text{CO})_8$, dodecarbonyl tetracobalt $\text{Co}_4(\text{CO})_{12}$, etc. These compounds can be used individually or in combinations.

Organic solvents suitable for the invention may comprise octane, nonane, decane, octene, nonene, decene, or similar lower aliphatic hydrocarbons, toluene, xylene, mesitylene, ethylenebenzene, tetralin, or similar lower alkylbenzenes, butanol, pentanol, hexanol, octanol, decanol, 2-methoxyethanol, 2-ethoxyethanol, oleyl alcohol, benzyl alcohol, or similar substituted or unsubstituted lower-aliphatic and aralkyl-primary alcohols, butylether, anisole, or similar lower aliphatic or aromatic ethers, diethyl ketone, methylisobutyl ketone, cyclohexanone, or similar lower aliphatic and alicyclic ketones, propyl acetate, butyl acetate, pentyl acetate, or similar ester acetates, and chlorobenzenes, cyclobenzenes, or similar halogen substituents of the aforementioned organic solvents. These compounds can be used individually or in combinations.

The use of secondary alcohols is not desirable since a superfine metallic cobalt powder cause their dehydration.

Materials suitable for the reactor or for the reactor linings can be selected from the following compounds: tetrafluoroethylene resin, trifluoroethylene chloride, a copolymer of tetrafluoroethylene and perfluoroalkylvinylether, a copolymer of tetrafluoroethylene and hexafluoropropylene, a copolymer of tetrafluoroethylene and ethylene, a copolymer of trifluoroethylene chloride and ethylene, or similar

resins of low polarity suitable for continuous operation at a temperature exceeding 100°C. Other materials may comprise aluminum, stainless steel, copper, or the like. These materials can be used individually or in combinations.

A composition prepared for manufacturing a superfine metallic cobalt powder may contains 5 to 1000 parts by weight of an organic solvent recalculated for 1 part by weight of metallic cobalt contained in a cobalt carbonyl compound.

A method of thermal decomposition of a cobalt carbonyl compound consists of loading of appropriate amounts of an organic solvent and a cobalt carbonyl compound into a stirrer, condenser, a reactor equipped with an inert-gas supply system, or a similar piece of equipment made from an inert material, then filling the equipment with inert gas such as argon, nitrogen, etc., and carrying out a thermal decomposition reaction by heating the contents. It is recommended that the reaction temperature be within the range of 110 to 200°C. A temperature below 110°C is impractical since the reaction will be significantly delayed. Since such conditions require the use of an organic solvent with the boiling point below 110°C, the thermal decomposition reaction should be conducted under an increased pressure.

In an alternative method, first only a part of the cobalt carbonyl compound is loaded to the reactor, and another part of the aforementioned compound is added in the form of a solution or a slurry in a preheated organic solvent for subsequent thermal decomposition.

The superfine metallic cobalt powder obtained by the method of the invention precipitates or partially disperses in the organic solvent and can be easily converted into a uniform dispersion by shaking.

The average size of superfine metallic cobalt powder particles in the dispersion will depends on the type of the organic solvent and thermal decomposition conditions of the process, but, the higher is the thermal decomposition temperature for the same solvent, the smaller is the size of the obtained particles. Normally, the particles are obtained with the dimension of 100 to 5000 Å.

(e) Practical Examples

Practical Example 1

A 1-liter reactor made from a tetrafluoroethylene resin and equipped with a stirrer, a condenser, and a gas-supply port made from the same resin was filled with 58 g of octacarbonyldicobalt $\text{Co}_2(\text{CO})_8$ and 500 g of toluene. The reactor was filled with nitrogen, the temperature was increased, and refluxing was carried out with stirring (reaction temperature was 110°C). At the moment when generation of carbon monoxide was discontinued, the reaction was stopped (duration of the reactor was 5 hours), and the reactor was cooled. Observation of the superfine metallic cobalt powder in the obtained suspension under a transition electronic microscope (the same microscope was used also in other practical examples) showed that the particles had an average diameter of 1400 \AA . A picture of the particles obtained in Practical Example 1 taken with the use of the transition electronic microscope is shown in Fig. 1 ($\times 5 \times 10^4$).

Practical Examples 2 to 7

Superfine metallic cobalt powder suspensions were obtained by the same reaction as in Practical Example 1 but under conditions indicated in Table 1. The same table shows the average diameter of particles in the obtained superfine metallic cobalt powder. Figs. 2, 3, and 4 show pictures of particles obtained in Practical Examples 2, 3, and 4 taken with the use of the transition electronic microscope with multiplication of $\times 5 \times 10^4$.

Comparative Examples 1 to 7

Superfine metallic cobalt powder suspensions were obtained by the same reaction as in Practical Example 1 but under other conditions that are indicated in Table 1 and in a reactor made from glass.

In all Comparative Examples 1 to 7, the metallic cobalt formed a mirror-like deposit on the inner walls of the glass-made reactor. The cobalt peeled off from the reactor walls admixed with the superfine powder suspension, and therefore it was impossible to obtain a suspension of high purity.

Practical Example 8

A 1-liter reactor made from stainless steel and equipped with a stirrer, a condenser, and a gas-supply port made from stainless steel was filled with 58 g of octacarbonyldicobalt $\text{Co}_2(\text{CO})_8$ and 500 g of xylene. The reactor was filled with nitrogen, the temperature was increased, and refluxing was carried out with stirring (reaction temperature was 140°C). At the moment when generation of carbon monoxide was discontinued, the reaction was stopped (it had a duration of 4 hours), and the reactor was cooled. The inner walls of the reactor were free of any mirror deposits of metallic cobalt. Observation of the superfine metallic cobalt powder in the obtained superfine metallic cobalt powder suspension under a transition electronic microscope showed that the particles had an average diameter of 700 Å.

Table 1

	Organic Solvent	Reaction Temperature ($^\circ\text{C}$)	Reaction time (Hr)	Average Particle Diameter (Å)
Pr. Ex. 1	Toluene	110	5	1400
Pr. Ex. 2	Mixed xylene	140	4	700
Pr. Ex. 3	n-Butanol	117	5	800
Pr. Ex. 4	n-Butyl acetate	126	5	500
Pr. Ex. 5	Nonane-1	147	4	1200
Pr. Ex. 6	Dibutyl ether	142	4	800
Pr. Ex. 7	Methylisobutyl ketone	117	5	800
Comp. Ex. 1	Toluene	110	5	-
Comp. Ex. 2	Mixed xylene	140	4	-
Comp. Ex. 3	n-Butanol	117	5	-
Comp. Ex. 4	n-Butyl acetate	126	5	-
Comp. Ex. 5	Nonane-1	147	4	-
Comp. Ex. 6	Dibutyl ether	142	4	-
Comp. Ex. 7	Methylisobutyl ketone	117	5	-

*Reaction conditions: 58 g of dicobalt-octacarbonyl $\text{Co}_2(\text{CO})_8$; organic solvent 500 g.

(f) Effects of the Invention

As the working surfaces of the reactors were made from inert materials that did not contain polar groups, it became possible to obtain superfine metallic cobalt powder suspensions without formation of mirror deposits on the aforementioned working surfaces and to produce aforementioned active suspensions without any adsorbed layers of organic polymer compounds and cobalt oxide layers on the surfaces of superfine particles of the metallic cobalt.

The obtained superfine metallic cobalt powder suspensions could be improved by adding small amounts various additives with molecular weight not exceeding 4000, such as non-ionic, amphoteric, anionic, or similar surface active agents, higher fatty acids, higher fatty acid amides, linseed oil, wood oil, soybean oil, coconut oil, etc.

Once the superfine metallic cobalt powder suspension is produced, the organic solvent can be replaced.

A superfine metallic cobalt powder suspension of high purity can be produced by removing the organic solvent from the suspension with the use of appropriate means.

4. Brief Description of the Drawings

Figs. 1, 2, 3, and 4 are respective pictures of superfine metallic cobalt powder particles of Practical Examples 1, 2, 3, and 4 obtained with the use of a transition electronic microscope (with magnification of 5×10^4).

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Fig. 1

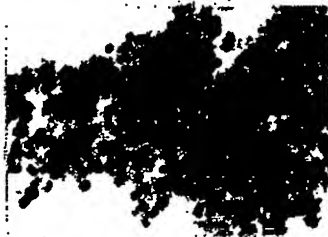


Fig. 2



Fig. 3

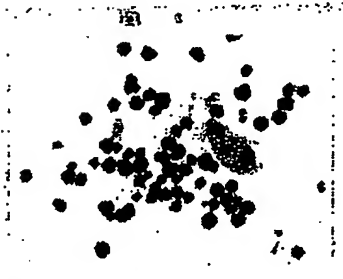


Fig. 4



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